

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 378 295
A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90300050.3

(51) Int. Cl.⁵: D06M 15/432, D06M 13/288

(22) Date of filing: 03.01.90

(30) Priority: 04.01.89 GB 8900060

(43) Date of publication of application:
18.07.90 Bulletin 90/29

(84) Designated Contracting States:
BE CH DE DK ES FR GB GR IT LI LU NL

(71) Applicant: Albright & Wilson Limited
210-222 Hagley Road West
Oldbury Warley West Midlands B68 0NN(GB)

(72) Inventor: Black, Robert William
104 Norman Road
Warley West Midlands B67 5PU(GB)

(74) Representative: Wilson, Michael John et al
c/o Albright & Wilson Limited 1
Knightsbridge Green
London SW1X 7QD(GB)

(54) Flame retardant composition and method of use.

(57) Aqueous compositions imparting semi durable flame retardant properties to fabrics from cellulosic and synthetic polymer fibres contain an ammonium or organic quaternary ammonium condensed phosphate and a cyclic organic phosphonate and preferably a carbamic acid derivative such as urea.

EP 0 378 295 A2

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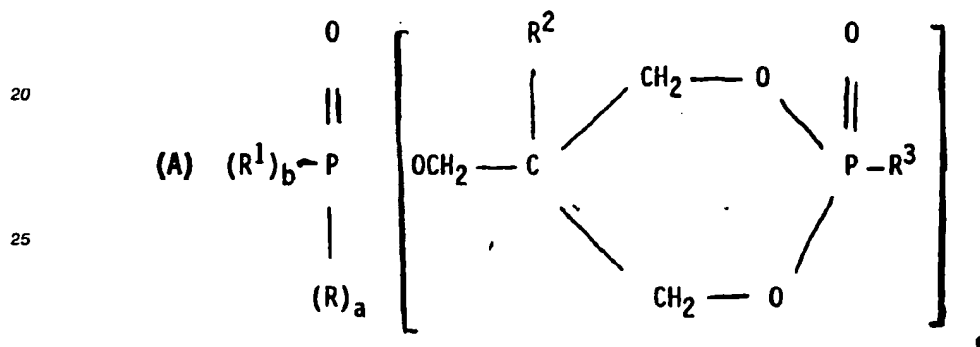
FLAME RETARDANT COMPOSITION AND METHOD OF USE

This invention concerns flame retardant compositions and methods of rendering textile substrates flame retardant with them.

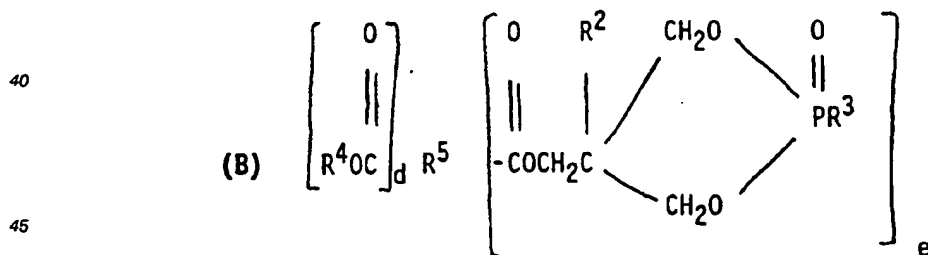
Cotton fabrics can be rendered flame retardant by incorporation therein of a wide variety of chemicals, some of which provide durable flame retardance and some of which provide non durable retardance. Among the latter chemicals is ammonium phosphate and polyphosphate optionally with added urea. While such compounds are cheap, their effectiveness is short lived as they are removed by washing with water. Attempts to increase the durability with such compounds included high temperature curing at above 150 °C (see e.g. GB-P 1504507). The curing of the polyphosphate can be associated with cocuring of a variety of usual fabric treatments agents e.g. dimethylolethylene urea (see e.g. GB-P 1069946). Cotton polyester fabrics especially union fabrics are more difficult than cotton fabrics to render even semidurably flame retardant.

We have discovered flame retardant compositions and processes for applying them to fabrics of cellulosic and other materials to give fabrics of increased durability of flame retardant.

The present invention provides a flame retardant composition comprising an ammonium or organic quaternary ammonium condensed phosphate and at least one cyclic phosphonate ester I of formula (A)



wherein a is 0, 1 or 2; b is 0, 1 or 2; c is 1, 2, or 3 and a+b+c is 3; R and R' are the same or dissimilar and are alkyl, alkoxy, aryl, aryloxy, alkaryl, alkaryloxy, aralkyl, aryloxyalkoxy, or aralkoxy wherein the alkyl portion of these groups may contain at least one hydroxyl but not halogen and the aryl portion may contain at least one chlorine, bromine or hydroxyl group; R² is alkyl, hydroxyalkyl, or aryl; R³ is lower alkyl (e.g. C₁-C₄), or hydroxyalkyl (e.g. C₁-C₄), or cyclic phosphonate ester of formula (B)



where d is 0, 1 or 2; e is 1, 2 or 3; d+e is 3; R² is as defined above; R³ is defined above; R⁴ is alkyl, aryl, alkaryl, aralkyl, or aryloxyalkyl, wherein the aryl portion may optionally contain at least one bromine, chlorine or hydroxyl; and R⁵ is monovalent, divalent or trivalent alkyl, alkylene, aryl or arylene radical wherein the aryl or arylene radical may optionally contain at least one bromine, chlorine, alkyl or hydroxyl group. The composition may also contain an aqueous-dispersible fluoropolymer but preferably contains a carbamic acid derivative eg urea.

The present invention also provides a method of flame retarding a fabric which comprises impregnating

a union fabric having cellulosic and noncellulosic fibres with an aqueous medium comprising the flame retardant composition of the invention, and then drying and curing at a temperature of 130 - 180 °C.

The polyphosphate salt may be made by reaction of a condensed phosphoric acid with ammonia or an organic amine or quaternary ammonium hydroxide to give a water soluble product. The condensed phosphoric acid usually has a mean degree of condensation of more than 3, e.g. 3-30, and usually has a linear, branched or cyclic structure. Preferably the salts contain N and P in an atomic ratio of 0.5-2:1 especially about 1:1. The polyphosphate salt is preferably a mixture of the ammonium salts of a plurality of polyphosphoric acids, which mixture has been produced by a process of reacting an aqueous solution of phosphoric acids containing 80-86% by weight of phosphorus pentoxide with ammonia or a basic derivative thereof at a temperature of 15-70 °C e.g. 15-40 °C and at a pH of 4-12 e.g. 5-9 e.g. 6.5-7.5, or 5 to 12 especially 6 to 8. Ammonium polyphosphate mixtures which may be used are described in GB-P-1504507 and may be made as described therein.

The cyclic phosphonate ester I is described in USP3849368 and 3789091, the disclosures of which are hereby incorporated by reference. It may be made as described in these patents by reaction of alkyl halogen free esters of phosphorus acids or carboxylic acids or sulphonic acids, with a bicyclic phosphite e.g. a 1-alkyl-4-phospha-3.5.8-trioxa bicyclo- [2,2,2] octane. Alkyl, alkoxy or substituted alkyl groups for R and R¹-R⁵ may contain 1-6 carbons, while aryl groups may be aromatic hydrocarbyl groups and may contain 6-19 carbons and aralkyl groups may be hydrocarbyl groups and may contain 7-19 carbon atoms. Examples of R and R¹ are C₁₋₆ alkyl, phenyl, halophenyl, hydroxyphenyl, tolyl, xylyl, benzyl, phenethyl, hydroxy ethyl, phenoxyethyl and dibromo phenoxy methyl. Examples of R⁴ are C₁₋₄ alkyl, phenyl, halophenyl, hydroxyphenyl, hydroxyethyl, phenoxyethyl, dibromo phenoxy - ethyl, tolyl, xylyl, benzyl or phenethyl while examples of R⁵ are monovalent C₁₋₆ alkyl, chlorophenyl, mono-, di- or tri- bromo-phenyl, hydroxy phenyl, naphthyl, tolyl, xylyl, benzyl or phenethyl; divalent C₁₋₆ alkylene, vinylene, o-, m- or p-phenylene, tetra chloro- or tetrabromo-phenylene (o, m or p) and trivalent phenenyl. Preferred compounds II are ones in which each of R and R¹ which may be the same or different represents a lower alkyl or lower alkoxy group eg of 1-6 carbons, especially 1-3 carbons, especially methyl, ethyl, methoxy and ethoxy, while each of R² and R³ which may be the same or different, preferably represents an alkyl group eg of 1-6 carbons such as a methyl or ethyl group. Mixtures of the cyclic phosphonates may be used, such as ones with 95:5 to 5:95 eg 25:75 to 75:25 proportions of 2 phosphonates, especially a first phosphonate wherein each of a, b and c is 1, and a second phosphonate wherein a is 1, b is 0 and c is 2, each of the groups R, R² and R³ independently in one phosphonate being otherwise the same as the corresponding group in the other phosphonate.

The most preferred mixtures are 40:60 to 60:40 mixtures of these two phosphonates wherein each of R, R² and R³ represents a methyl or ethyl group and R¹ represents methoxy or ethoxy such as in Ex.1b of USP3849368 especially wherein R and R³ are methyl, R² is ethyl and R¹ methoxy; an example of such a mixture is the 50:50 w/w mixture (wherein R, R³ are methyl R¹ methoxy and R² ethyl) sold by Albright & Wilson Americas Inc under the Registered Trade Mark ANTIBLAZE 19 or by Albright & Wilson Ltd under the Registered Trade Mark AMGARD CU. The weight proportion of cyclic phosphonate to the ammonium polyphosphate is usually 0.1-2:1 such as 0.3-1.0:1 or 0.4 - 1.3:1.

The flame retardant medium usually contains a carbamic acid derivative having 2 amino groups per molecule in a weight percentage (expressed as urea) to the ammonium polyphosphate (expressed by weight as ammonium polyphosphate itself) of 0.5%-300% such as 0.5-50% eg 5-30% such as 7-20% or 10-20%, while 50-300% e.g. 50-200% and especially 75-125% are preferred, particularly for higher temperature curing; generally the higher the cure temperature the higher the proportion of carbamic acid derivative. The carbamic acid derivative may be guanidine or dicyandiamide, but is preferably urea; the weights are expressed as urea but equivalent weights of the other carbamic acid derivative can be used. The presence of the carbamic acid derivative reduces any tendency to discoloration of the fabric after heat curing, especially at high temperature, and may increase the wet pick up.

The flame retardant medium also may contain a dispersion of fluorocarbon polymer (capable of being heat cured at more than 160 °C eg 160 °C-200 °C). The fluorocarbon polymer is one which forms in the flame retardant medium a dispersion which is usually stable for at least a few days e.g. at least 2 days; thus fluoropolymers incompatible with the condensed phosphate and cyclic phosphonate solution (with carbamic acid derivative if present) and forming precipitates on mixing therewith are avoided. The medium is usually substantially free of other heat curable water soluble resins or resin precursors such as formaldehyde condensates with NH compounds such as melamine, urea or ethylene urea. Such aqueous dispersible polymers usually have perfluoro alkyl side chains e.g. in perfluoro-acyl, -sulphonyl or-sulphonamido groups, especially ones with 3-12 carbon atoms in the perfluoroalkyl group; carboxy groups may be present. The fluorocarbon polymers are preferably derived from acrylic or methacrylic esters of hydroxy compounds

containing perfluoro alkyl groups but can be derived from vinyl esters, vinyl ethers, allyl esters or thiomethacrylates with perfluoro-alkyl side chains. Especially preferred polymers are ones containing (N-alkyl N-perfluoroalkylsulphon-amido) alkylene side chains e.g. 2- (N- propyl N- perfluorooctylsulphonamido) -ethylene side chains with an acrylate or methacrylate ester backbone. The polymers may be made only from monomers containing perfluoro alkyl groups but these monomers may have been copolymerized with other copolymerizable monomers particularly ones fluorine free e.g. ones containing one or especially two olefinic double bonds e.g. as in halo butadienes such as 2-chloro 1,3-butadiene. Olefinic monomer units containing carboxylic acid groups e.g. acrylic, methacrylic or maleic acid groups may be present in the polymer. The fluoro polymers are usually sold in the form of aqueous dispersions eg for fluoropolymer soil repellent finishes for fabrics. The polymer dispersion may be non ionic but is preferably cationic or especially anionic. The fluoropolymer dispersions may also contain small amounts of water miscible organic solvents e.g. acetone, MIBK or ethylene glycol. A preferred fluoropolymer dispersion is that sold by 3M Company under the trademark SCOTCHGARD 270 or by Ciba Geigy under the trademark SCOTCHGARD FC451. This polymer is believed to be a copolymer of an 2 (N-alkyl N-perfluoro octylsulphonyl amido) ethyl acrylate and a comonomer probably 2-chloro -1, 3,- butadiene. Another preferred fluoropolymer dispersion is that sold by Hoechst AG under the trademark NUVA FH or NUVA F; fluoropolymer dispersions sold by Atochem SA under the trademark FORAPERLE especially FORAPERLE 145 and 344, or Texchem UK Ltd Manchester England under the trademark TEXFIN CPC may also be used. The weight percentage of fluoro polymer (solids) to ammonium polyphosphate is usually 0.1-6% e.g. 1-3% but especially 2-6%.

The flame retardant medium usually contains 7-18% e.g. 7-13 or 8-15% such as 9-13% ammonium polyphosphate, and 1-20% eg 3-10% or 5-10% of the cyclic phosphonate and usually 7-18% e.g. 7-13 or 8-15% such as 9-13% of the carbamic acid derivative e.g. urea, and optionally 0.02-1.5% e.g. 0.1-1% and especially 0.3-0.8% fluoropolymer. However amounts of the ammonium polyphosphate of 7-24% such as 10-24% eg 15-24% and especially 15-23%, and amounts of 0-20% eg 1-20% or 0-15% eg 1-15% or 1-10% such as 1.5-4% of the carbamic acid derivative may be used. Advantageously the total content of the polyphosphate, carbamic acid derivative e.g. urea and fluoro polymer (if present) in the medium is not more than 26% e.g. 11-26% or 15-26% especially 20-24%.

The medium can also contain a non rewetting agent e.g. a volatile wetting agent such as an alcohol or an agent such as is sold by Warwick Chemicals under the trademark MYKON NRW; amounts of such non rewetting agents of 1-10g/l. are preferred. However if the substrate, which is to be flame retarded, has already been scoured or otherwise treated to aid penetration of liquids, then no such agent is required but one may be present if desired. Particularly when fluoropolymer is present the aqueous medium is usually in the absence of extenders or cationic polymers such as cationic synthetic resin waxes, such as are sold under the trademark CEROL by Sandoz, and is also usually substantially free of di, tri or tetra valent metal salts e.g. those of aluminium or zirconium. Some fluoropolymer dispersions are sold which contain also the extender or cationic polymer; these should preferably not be used. Fluoropolymer dispersions sold primarily to provide soil repellency, but not to provide soil and water repellency, are preferred as the latter tend to contain the cationic polymer and may be incompatible with the concentrated polyphosphate solution.

In preferred embodiments, the flame retardant composition is an aqueous medium comprising 7-15% e.g. 8-13% by weight of an ammonium or organic quaternary ammonium condensed phosphate, 3-10% by weight of the cyclic phosphonate preferably ones of formula II (and especially mixtures thereof) 7-15% by weight of carbamic acid derivative e.g. urea, the weight percentage of urea to polyphosphate being 50-200%, with a total content of the phosphate and urea of not more than 25%. These compositions are preferably in the absence of cationic water soluble fluorine free polymers, and advantageously may contain the fluoropolymer which has perfluoroalkylsulphonamide side chains.

The polyphosphate, preferably with the carbamic acid derivative, may be provided as a concentrated aqueous solution for subsequent mixing with the cyclic phosphonate before or preferably after one or both has been diluted to the strength for the impregnation bath.

If the fluoropolymer is to be present in the medium the fluoropolymer dispersion is preferably added to the medium when it is otherwise ready for use for impregnation and the medium is preferably used for impregnation within a few days though, especially in the case of anionic fluoropolymer dispersions, the medium may be stable for months at least 1 wash eg at least 1 month.

The aqueous medium may also contain other textile auxiliary agents of nature and in amount such that they are compatible with the other components of the medium, and are not significantly affected by the heat cure treatment e.g. to cause discoloration or loss of effect. Examples of such agents are softening or conditioning agents, which may be cationic, anionic, non ionic, amphoteric or reactive, and usually contain at least 1 and often 2 alkyl chains of at least 10 carbon atoms.

Examples of cationic softening agents are fatty quaternary ammonium salts, amino esters and amino

amides and quaternary N acyl N polyoxyalkylene polyamines. Examples of anionic softening agents are fatty acid salts, soaps, sulphonated fats and oils, fatty alkyl sulphates and fatty acid condensation products, sulphosuccinates and sulphosuccinamates. Examples of amphoteric agents are alkyl imidazolines and betaines and salts thereof e.g. methosulphate, acyl amido betaines, acyl polyamines, amine oxides, substituted amino acids and sulpho betaines. Examples of non ionic softening agents are poly alkylene glycol ethers and esters and other polyoxyalkylene condensation products, and paraffin wax or polyethylene wax, these latter two being used in aqueous dispersion or emulsion, with non ionic cationic or anionic but especially amphoteric dispersing agents. Examples of reactive softening agents are N-methylol derivatives of fatty acid amides e.g. N-methylol stearamide or N methylol derivatives of fatty acid condensates with urea. The softening agent as such or as dispersion thereof may be used in amount of 0.01-5% e.g. 0.5-3% by weight of the total aqueous impregnation medium. The presence of the softening agent can enable the heat cure process to produce a treated fabric having improved flame retardance and with other properties e.g. strength especially tear strength and colour substantially the same as those of the untreated fabric; the strength may even be improved.

The substrates to which the medium is applied may be woven or non woven. They are cellulosic based substrates e.g. textile fabrics, such as cotton, linen, jute, hessian or regenerated cellulosic materials, such as rayon or viscose, with other fibres coblendable or mixable therewith e.g. polyester or nylon, acrylics, acetate, polypropylene, silk or wool; these blends or mixtures of fibres may contain at least 30% such as 30-100% or 30-90%, but preferably at least 40% such as 40-75% and especially at least 50% of the cellulosic material such as 50-90%, 50-80% or 70-90% thereof.

Preferred are fabrics from non blended mixtures of cellulosic material eg cotton and synthetic polymer eg polyester or nylon. The fibres used to form at least part of the fabrics may if desired be of core sheath construction but are preferably not so. The fabrics are of union construction, for example with at least one of the weft and especially the warp being predominantly (eg 50-100%), especially essentially completely, of synthetic polymer fibres such as with a warp predominantly of polyester; polyester or nylon warp and cotton weft especially with embossed cotton designs are preferred. In the absence of the cyclic phosphonate application of flame to such union fabrics may tend to cause the polyester to shrink back and melt separately from the cotton and then burn, thus reducing the overall effectiveness of the flame retarded fabric when for example used in upholstery. The flame retardant compositions of the invention and the method of the invention enables one more uniformly to flame retard at least semidurably such union fabrics preferably embossed ones but especially ones with non uniform distribution of synthetic polymer and cellulosic material on a surface thereof hereinafter called "differential surface fabrics". Particularly important differential surface fabrics are ones with a front side with a different (usually lower) proportion of the cellulosic material to synthetic material from that on the back side, as well usually as having a face or front side having significant areas of predominantly (eg 50-100%) fibres of synthetic polymer on the surface, as well usually as significant areas of predominantly (eg 50-100%) fibres of the cellulosic material. Examples of such differential surface fabrics are ones with a polyester warp and dyed cotton weft, especially with more than one differently coloured cotton weft, with the fabrics woven with front designs of such dyed cotton on a background of the polyester warp and a nondesigned back with a substantial cotton surface. Such differential surface fabrics may be used as upholstery fabrics.

Fabric weights can be 0.050-1.0kg/m², e.g. 0.080-0.500kg/m². Each of the components of the fabric may be plain or undyed or may be dyed especially with white or pastel shades. The fabric before impregnation is usually free of dirt, sizes, natural waxes and applied finishes though may contain an optical brightening agent.

The flame retardant medium usually at pH 5-8 e.g. 5.5-7.5 is applied to the substrate by conventional procedures e.g. padding, soaking or spraying usually to a wet pick up of 50-150% e.g. 60-100%. The total solids add on before drying and after squeezing off surplus liquid is usually 10-35% e.g. 10-20% or 13-25% (based on the dry initial weight of the fabric). After impregnation the substrate is then dried e.g. for textile substrates at 80-120°C for 2 to 40 minutes e.g. 2-10 minutes. The drying may be performed in any conventional drier e.g. a forced air drier or stenter. The solids pick up after drying is usually 8-25% such as 10-20% (based on the original weight of the fabric).

The dried substrate is then cured eg by heating at a temperature of at least 130°C such as at least 140°C e.g. 140-180°C such as 140-170°C, 140-165°C or 147-170°C e.g. for 6 to 0.5 minutes, the combination of longer times and higher temperature being avoided to decrease any tendency to discoloration. Thus preferred temperatures are 147-165°C such as 147-160°C or 147-155°C for 6-0.5 e.g. 5-2 minutes, though 138-147°C for 3.5-0.5 minutes can be used. The presence of any fluoropolymers in the impregnation medium and hence the fabric can increase the durability of flame retardancy to soaking of the fabric, and can increase the soil resistance of the fabric.

The curing which is usually continuous may be performed by radiant e.g. infra red heating or heating by injection of steam and/or hot air through the substrate, or by contact of the substrate with heated metal drums in a vertical stack, but preferably the curing is by heating from impact of hot air on the surface of the substrate, preferably on both surfaces to ensure uniformity of heating. Thus preferably the substrate is passed continuously on a stenter through a thermostated oven in which heated air flows are passed on to the top and bottom surfaces of the substrate. The stenter gives the most uniform curing with minimum scorching. In the case of the stenter oven, the cure temperature of the substrate is essentially the same as that of the heated air flow. Usually at the end of the curing the substrate is cooled rapidly by passing or drawing cool air through it.

The cured fabric as finished usually has a solids content of 6-25% such as 8-20% and usually contains 0.5-4% preferably 1-3%P or 2-4%P. The fabric as finished has a reduced flammability compared to the untreated substrate and can pass the BS 5852 test with ignition sources 0 and 1. The fabric after leaching once in hard water at 40° C according to BS 5651 without final ironing usually has a solids content of 3-10% e.g. 4-9%, a % P content of 0.4-3% preferably 0.9-3% e.g. 1-3% and can pass the flammability test of BS 5852 Part 1 with ignition sources 0 and 1. The reduced flammability finish is usually durable for 1-3 washes in soft water at 74° C while some fire retardant effect is retained thereafter. The fabric as finished usually has a handle not significantly changed from that of the untreated fabric, and usually has a colour not significantly changed from that of the untreated fabric.

The synergistic combination of the (i) polyphosphate salt and (ii) cyclic phosphonate, especially with the carbamic acid derivative, can give treated fabrics with improved flammability and durability thereof not possessed by fabrics treated by (i) or (ii) alone.

The invention is illustrated in the following Examples. The fluoropolymer if present was used as a 23% aqueous emulsion of fluoropolymer with a slight cationic character sold by 3M under the Trademark SCOTCHGARD FC 208 or Ciba Geigy under the Trademark SCOTCHGARD FC451. This fluoropolymer is believed to be a copolymer of 2 (N-propyl N- perfluoro octylsulphonyl amido) ethyl acrylate and 2-chloro- 1, 3- butadiene. The ammonium polyphosphate used was made by reacting polyphosphoric acid of 83-85% P₂O₅ with ammonia according to GB-P 1504507, to produce a product which was adjusted to give a solution at pH6.2 containing 45% solids, 30% P₂O₅ and a specific gravity of 1.36.

The cyclic phosphonate was an 50:50 mixture of cyclic phosphonates sold under the Trade Mark ANTIBLAZE 19 or AMGARD CU (as described above). The softening agent was an aqueous amphoteric dispersion of an aliphatic hydrocarbon, probably a paraffin wax or polyethylene wax, sold by Sandoz under the Trade Mark SANDOLUBE NV.

In each case the same general procedure was adopted. The aqueous solution of the ammonium polyphosphate, urea and cyclic phosphonate if present was made and after dilution with water as desired, was mixed with stirring with the softening agent in amount of 2% (based on the total weight of impregnation medium), fluoropolymer emulsion, if present, in amount of 2% by weight of emulsion based on the total weight of solution and emulsion, and also 0.5% of a non rewetting agent sold under the trade mark MYKON NRW to give aqueous media containing the ammonium polyphosphate, urea, wetting and softening agent, and if present cyclic phosphonate and/or fluoropolymer. The aqueous medium obtained was stable, but was preferably used without undue delay especially when fluoro polymer was present. Each fabric, which was an upholstery fabric, was impregnated with the aqueous medium and squeezed and then the impregnated fabric dried at 90-100° C for 1 minute in a forced air drier or stenter. Portions of the dried fabric were then moved on a stenter slowly but continuously through a thermostated stenter oven provided with heated air flows impinging on the fabric from top and bottom. The cured fabric was then tested according to the test of BS 5852 Part 1 with ignition sources 0 and 1 for flammability as finished and after leach once in hard water at 40° C according to BS 5651 Part 1 without final ironing.

Example 1 - 6 and Comparative Ex A-F

In Ex 1-6 the aqueous ammonium polyphosphate solution (59 parts) and urea (27 parts) and water (139 parts) were mixed and then the cyclic phosphonate (15 parts), fluoropolymer emulsion, softening agent and wetting agent added to give the impregnation medium. The medium was applied in a pad mangle to each of 6 cotton polyester union fabrics of 0.270kg/m², with wet pick-ups of about 80% respectively. The fabrics were of 85% dyed cotton weft and 35% polyester warp and were obtained from 3 suppliers. The fabrics had different wearing styles with different proportions of polyester to cotton on their faces and different proportions of polyester to cotton on their backs. Fabrics A and B had substantially uniform distribution of polyester to cotton on their faces while in Fabrics C, D, E and F the dyed cotton was

present on the face in many places in an upraised design set on a polyester background while on the back the surface fibres were predominately of the dyed cotton. The impregnated fabrics were then dried on a forced air stenter at 100 °C for 1 minute and then cured at 150 °C for 3 minutes in that stenter. All the fabrics as finished and after one leach in hard water passed the BS 5852 test with ignition sources 0 and 1.

- 5 In Comparative Ex A-F the process were repeated without the cyclic phosphonate. All the fabrics after the one leach in hard water failed the BS 5852 test with ignition sources 0 and 1, fabrics C-F being substantially instantly ignited.

10 Examples 7-15 and Comparative G-O.

The processes of Examples 1-6 were repeated without the fluoropolymer emulsion but with different union fabrics, and different proportions of cyclic phosphonate.

- 15 The wet pickup was about 80% but the amount of added water in the impregnation medium was adjusted so that in each case there was an essentially constant uptake on the fabric of the ammonium polyphosphate and urea (namely 6.9% ammonium polyphosphate and 7.0% urea solids respectively). The nature of the fabric and weight of the cyclic phosphonate applied to the fabric were as given in the table below. Each fabric had a cotton weft and polyester warp with an upraised dyed cotton warp and weft design in the face set on a polyester background with a significant area of the polyester warp exposed, but the average proportion of polyester to cotton on the face paralleled that in the fabric overall. The conditions of drying and curing were as for Ex1-6. The fabrics as finished and after one leach in hard water all passed the flammability tests before and after leach. In comparative Ex G-O, the experiments were repeated without the cyclic phosphonate and all failed the BS 852 test after the water leach.

25	EX	POLYESTER/COTTON%	WT%PHOSPHONATE ON FABRIC	FABRIC WEIGHT KgM ⁻²
	7	30:70	5.4	0.320
30	8	30:70	5.4	0.400
	9	30:70	5.2	0.440
	10	35:65	5.6	0.380
	11	35:65	5.4	0.420
	12	39:61	5.8	0.340
35	13	46:54	5.2	0.520
	14	49:51	6.5	0.300
	15	50:50	6.0	0.550

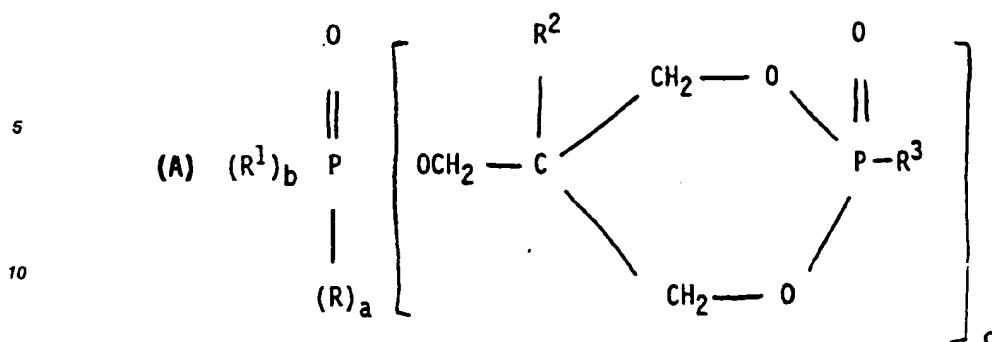
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Claims

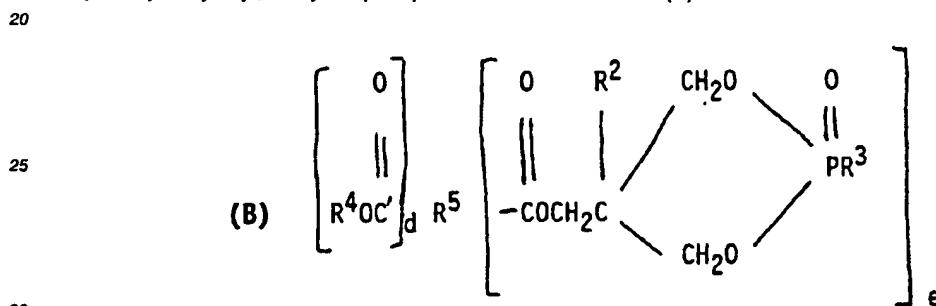
- 45 1. A flame retardant composition comprising an ammonium or organic quaternary ammonium condensed phosphate and at least one cyclic phosphonate ester of formula (A)

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wherein a is 0, 1 or 2; b is 0, 1 or 2; c is 1, 2, or 3 and a + b + c is 3; R and R¹ are the same or dissimilar and are alkyl, alkoxy, aryl, aryloxy, alkaryl, alkaryloxy, aralkyl, aryloxyalkoxy, or aralkoxy wherein the alkyl portion of these groups may optionally contain at least one hydroxyl but not halogen and the aryl portion may contain at least one chlorine, bromine or hydroxyl group; R² is alkyl, hydroxyalkyl, or aryl; R³ is lower alkyl or hydroxyalkyl, or cyclic phosphonate ester of formula (B).



where d is 0, 1 or 2; e is 1, 2 or 3; d + e is 3; R² is as defined above; R³ is defined above; R⁴ is alkyl, aryl, alkaryl, aralkyl, or aryloxyalkyl, wherein the aryl portion may contain at least one bromine, chlorine or hydroxyl; and R⁵ is monovalent, divalent or tervalent alkyl, alkylene, aryl or arylene radical wherein the aryl or arylene radical may optionally contain at least one bromine, chlorine, alkyl or hydroxyl group.

2. A composition according to claim 1 which comprises an ammonium polyphosphate.

3. A composition according to claim 1 or 2 wherein the cyclic phosphonate is of formula A, wherein each of R and R¹ represents a lower alkyl or alkoxy group of 1 - 6 carbon atoms and each of R² and R³ represent an alkyl group of 1-6 carbon atoms.

4. A composition according to claim 3 wherein each of R, R², and R³ represents a methyl or ethyl group and R¹ represents a methoxy or ethoxy group.

5. A composition according to claim 3 or 4 which comprises a 25-75:75-25 weight proportion of two phosphonates of formula A, one of which has a, b and c equal to 1 and the other of which has a equal to 1, b equal to 0 and c equal to 2.

6. A composition according to any one of the preceding claims wherein the weight proportion of the cyclic phosphonate to the condensed phosphate (expressed as ammonium polyphosphate) is 0.1-2:1.

7. A composition according to claim 6 wherein the proportion is 0.3-1.0:1.

8. A composition according to any one of the preceding claims which also comprises a carbamic acid derivative.

9. A composition according to claim 8 which comprises 50-200% of urea (based on the weight of the condensed phosphate, expressed as ammonium polyphosphate).

10. A composition according to any one of claims 3-9 which comprises 8-15% of ammonium polyphosphate, 3-10% of cyclic phosphonate and 8-15% of urea, with water.

11. A composition according to any one of the preceding claims, which also comprises a fluoroacrylic polymer in aqueous emulsion.

12. A method of flame retarding a fabric, which comprises impregnating a union fabric having cellulosic and non cellulosic fibres with an aqueous medium comprising a composition as claimed in any one of

claims 1 - 11, and then drying and curing at a temperature of 130 °C-180 °C.

13. A method according to claim 12 wherein the curing is at 140 °C-170 °C for 6-0.5 minutes.

14. A method according to claim 12 or 13 wherein the union fabric has 30-90% cellulosic fibres.

15. A method according to claim 12 or 13 wherein the union fabric has 50-80% cellulosic fibres and the
5 non cellulose fibres are of polyester or nylon.

16. A method according to claim 12, 13, or 15 wherein the union fabric has a warp predominantly of
polyester.

17. A method according to claim 12, 13, or 15 wherein the fabric has a cotton weft with an embossed
cotton design and a polyester warp.

10 18. A method according to any one of claims 12-17 wherein the fabric is a differential surface fabric.

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